

PATENT SPECIFICATION

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(54) METHOD OF PRODUCING POLYAMIDES

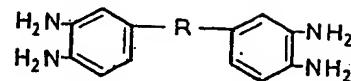
(71) We, BURYATSKY INSTITUT ESTESTVENNYKH NAUK, a Corporation organised and existing under the Laws of the Union of Soviet Socialist Republics of 35 5 Kirova, Ulan-Ude, Union of Soviet Socialist Republics do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in 10 and by the following statement:—

The present invention relates to the production of polymers. More particularly, the invention is concerned with polyamides possessing improved light and heat resistance.

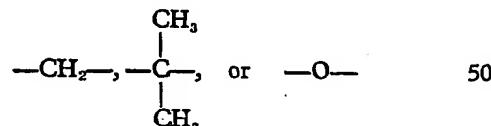
20 Copolymers containing both benzoxazole and amide structures have been previously disclosed in British Patent No. 811,758. The polymers disclosed in that Patent are, however, characterised as being polybenzoxazoles, 25 the copolymerisation therein of monomers such as hexamethylenediamine/dicarboxylic acid being an optional modification thereof. In contrast, the present invention is concerned with polymers which are characterised as 30 being polyamides of hexamethylenediamine and a dicarboxylic acid, heterocyclic structures being introduced in an amount sufficient only to enhance the stability of such polymers against light, heat and hydrolysis, but insufficient to change their character and field of 35 application from those of polycarbonamides of hexamethylene diamine to those of polybenzoxazoles.

40 According to the present invention there is provided a method of producing a polyamide by the polycondensation of a mixture of hexamethylenediamine and a dicarboxylic acid or its diphenyl ester in the presence of up to 6% mol, based on total reactants, of 45 an aromatic tetra-amine of the general formula:—

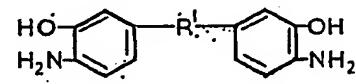
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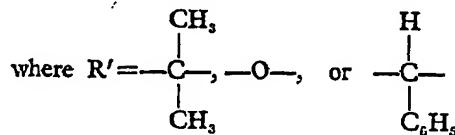
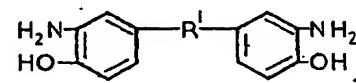
where R=a direct carbon to carbon valency link.



or an aromatic bis - o - aminophenol of the general formula:—



or



in a stream of inert gas while heating to 55 180—260° C.

To increase the molecular weight, the poly-

amide obtained may be additionally heated in vacuo (1 mm mercury) at 260—280° C.

5 A general method of producing polyamides according to the present invention is embodied as follows.

10 Before beginning the reaction of polycondensation, the initial components are thoroughly comminuted, mixed and charged into a condensation flask through which a clean inert gas is blown, the flask being alternately filled and evacuated. The reaction flask is then placed in a bath preliminarily heated to 180° C, after which the reaction mixture, which forms a melt, is heated to the temperature of the synthesis. The aromatic tetra-amine or bis - o - aminophenol may be added with the initial monomers or after the polyamide melt has formed.

15 Polyamides prepared in the presence of aromatic tetra-amines or bis - o - amino-phenols contain benzimidazole or benzoxazol groups. Said groups are more resistant to chemical reagents, light and heat than aliphatic groups. For that reason they impart 20 to polymers improved properties compared with the unmodified polyamides.

25 The polyamides manufactured, according to the present invention, can be used for lengthy periods at temperatures up to 150° C, possess 30 50—100% higher light resistance than polyamides now commercially available and are more resistant to concentrated mineral acids, e.g. they are only partially hydrolyzed by concentrated hydrochloric acid.

35 The method according to the present invention is illustrated by the following examples, in which the percentages given are percentages by weight unless otherwise stated.

EXAMPLE 1

40 A mixture of 1.05 of hexamethylene-diamine (0.009 mol), 3.00 g (0.01 mol) of diphenyl adipate and 0.21 g (0.00098 mol, or 4.9% mol. based on total reactants) of 3, 3' - diaminobenzidine is heated in a stream 45 of inert gas at 180—260° C for 3 hours. After the formation of a melt, the reaction is continued in vacuo (1 mm Hg) at 270° C for another 3 hours. The polyamide has an 50 inherent viscosity of 0.61 in tricresol (0.5% solution at 20° C). The polymer is crystalline and soluble in tricresol, formic acid and chloral hydrate.

EXAMPLE 2

55 A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine and 3.54 g (0.01 mol) of diphenyl sebacate is heated in a stream of inert gas at 180—250° C for 2 hours, whereupon 0.22 g (0.001 mol. or 5% mol. based 60 on the total reactants) of 3, 3' - diaminobenzidine is added and the reaction is continued for another 3 hours. The polyamide has an inherent viscosity of 1.02 in formic acid (0.5% solution in 90% formic acid

at 20° C). The polymer is crystalline and soluble in formic acid and tricresol.

65 The tensile strength of a film formed from the above polyamide is lowered 8.3% when exposed to the air and sunlight for four months in summer; the tensile strength of polyamide film produced by a prior art method is lowered 25% under the same conditions. The reduction in tensile strength of polyamide film produced in the presence of a bis - o - aminophenol, i.e. 4, 4' - dihydroxy-3, 3' - diaminodiphenylpropane (Example 4), in the same conditions is 7.8%. Said polyamide is partially hydrolyzed when acted on by concentrated hydrochloric acid at 80° C for one hour. When the hydrolysate is diluted with water, a polyamide is precipitated which has an inherent viscosity of 0.2 in formic acid (0.5% solution in 90% formic acid at 20° C). Judging by the results of thermogravimetric analysis, the loss in weight of said polyamide at 350° C is 7.3%, whereas the loss in weight of polyamide produced by the prior art method is 22.7%.

EXAMPLE 3

90 A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine, 3.54 g (0.01 mol) of diphenyl sebacate, 0.1 g (0.00044) mol of the tetra-amine of diphenyl methane and 0.15 g (0.00065 mol) of the tetra-amine of diphenyl oxide is condensed by the method described in Example 1. The mol. percentage of the last two compounds based on total reactants is 5.45. The inherent viscosity of the polyamide is 0.60 in tricresol (0.5% solution at 20° C). The polymer is crystalline and soluble in formic acid, tricresol and chloral hydrate.

EXAMPLE 4

95 A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine and 3.54 g (0.01 mol.) of diphenyl sebacate is heated in a stream of inert gas at 180—260° C for 3 hours, whereupon 0.24 g (0.00098 mol, or 4.95% mol. based on total reactants) of 3, 3' - diaminobenzidine is added and the reaction continued at 260—270° C for another 2 hours. The inherent viscosity of the polyamide is 0.51 in m-cresol (0.5% solution at 20° C). The polymer is crystalline and soluble in formic acid and tricresol.

EXAMPLE 5

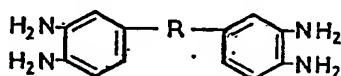
105 A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine, 3.00 g (0.01 mol.) of diphenyl adipate and 0.22 g (0.0009 mol. or 4.5 mol. % based on total reactants) of 3, 3' - diaminobenzidine is heated in a stream of inert gas at 180—260° C for 3 hours. After the formation of a melt the reaction is continued in vacuo

(1 mm Hg) at 265° C for another 3 hours. The inherent viscosity of the polyamide is 0.65 in m-cresol (0.5% solution at 20° C). The polymer is crystalline and soluble in m-cresol, tricresol and formic acid.

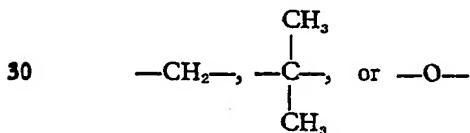
EXAMPLE 6
A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine, 3.54 g (0.01 mol) of diphenyl sebacate, 0.10 g (0.00043 mol.) of 3, 3' - diamino - 4, 4' - dihydroxydiphenyl methane and 0.14 g (0.00061 mol) of 3, 3' - diamino - 4, 4' - dihydroxydiphenyl oxide is condensed by the method described in Example 5. The mol. percentage of the last two compounds based on total reactants is 5.2. The inherent viscosity of the polyamide is 0.58 in m-cresol (0.5% solution at 20° C). The polymer is crystalline and soluble in m-cresol, tricresol and formic acid.

20 WHAT WE CLAIM IS:—

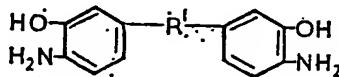
1. A method of producing a polyamide comprising the polycondensation of hexamethylenediamine and a dicarboxylic acid or its diphenyl ester in the presence of up to 6% mol, based on total reactants of an aromatic tetraamine of the general formula:—



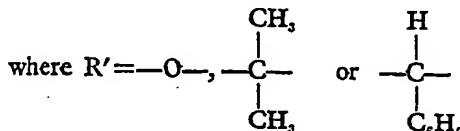
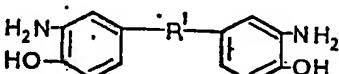
where R=a direct carbon to carbon valency link,



or an aromatic bis - o - aminophenol of the general formula:—



or



in a stream of inert gas while heating to 35
180—260° C.

2. A method as claimed in claim 1, wherein, after heating in a stream of inert gas, the reaction mixture is heated in vacuo at 260—280° C.

3. A method as claimed in claim 1 or 2, wherein the hexamethylenediamine and the dicarboxylic acid or its diphenyl ester are preheated to form a melt after which the tetra-amine or aminophenol is added.

4. A method as claimed in claim 1 or 2 wherein the tetra-amine or aminophenol is added with the hexamethylenediamine and the dicarboxylic acid or its diphenyl ester, and the mixture is subsequently preheated to form a melt.

5. A method of producing a polyamide substantially as hereinbefore described in any one of Examples 1 to 6.

6. A polyamide when produced by the 55 method as claimed in any preceding claim.

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